

# Single and solid solutions metal carboxyphosphonates as precursors for phosphorous-containing electrocatalysts.

A. Lopez-Vergara<sup>1\*</sup>, S.M. El-Refaei<sup>2</sup>, P. A. Russo<sup>2</sup>, A. Vilchez,<sup>1</sup> E.R. Losilla,<sup>1</sup> J.M. Porras-Vazquez,<sup>1</sup> P. Olivera-Pastor,<sup>1</sup> N. Pinna<sup>2</sup>, A. Cabeza<sup>1</sup>.

<sup>1</sup> Departamento de Química Inorgánica, Universidad de Málaga, Campus Teatinos s/n, Málaga-29071, Spain.

<sup>2</sup> Institut für Chemie and IRIS Adlershof, Humboldt-Universität zu Berlin, Brook-Taylor-Str. 2, 12489 Berlin, Germany.

(\*) Corresponding author: [adrliv@uma.es](mailto:adrliv@uma.es)

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## 1. Introduction

Nowadays, substitution of fossil fuels by new energy sources more respectful to the environment is becoming a priority due to the continuous growth of the population and the demand for energy. This makes renewable energies the only alternative for the subsistence of the planet in the medium-long term. This energy can be stored in chemical bonds, for instance by water splitting [1,2] and the generation of H<sub>2</sub> as energy carrier, which provides higher energy densities than other storage technologies such as Li-ion batteries.

Oxygen evolution reaction (OER) and Hydrogen evolution reaction (HER) are key steps for efficient energy conversion and storage technologies, which rely in the use of the scarce and expensive precious-metal materials, such as RuO<sub>2</sub>, IrO<sub>2</sub> and/or Pt. Recently, alternative materials, such as metal transition-based coordination polymers are receiving considerable attention as possible substitutes. In this context, metal phosphonates, consisting of extended structures formed by organophosphonate ligands coordinated to metal ions or clusters [3], are a type of versatile precursors to prepare efficient electrocatalysts by appropriate thermal treatments [4]. Heteroatom-containing metal pyrophosphates and metal phosphides can be obtained by pyrolysis, in which the selected metal ions can present a variety of coordination environments that influences dramatically the final electrocatalytic properties.

In this work, we report the preparation and characterization of potential water splitting electrocatalysts based on the mixed Co/Fe phosphonocarboxylates as precursor. The influence of different additives, such as graphene oxide (GO) and pyrazine, is also reported in relation to the possible structural changes and electrocatalytic effects after pyrolysis in H<sub>2</sub> atmospheres.

## 2. Experimental

### 2.1 Preparation of Co<sub>1-x</sub>Fe<sub>x</sub>HPAA (x= 0, 0.3, 0.7, 1) (HPAA= H<sub>3</sub>O<sub>2</sub>P-CH(OH)-COOH)

Taking advantage of the fact that isostructural compounds for Co(II) and Fe(II) [5] can be formed, different stoichiometric solid solution have been prepared. The mixed compounds were prepared by refluxing the corresponding amounts of CoSO<sub>4</sub> and FeSO<sub>4</sub> together with the HPAA ligand (metal: ligand molar ratio = 1:1) in an aqueous solution for 1 day. The obtained precipitate was filtered, washed with ethanol and finally dried at 60°C.

GO-containing samples were prepared by adding a suspension of ultrasonicated GO (0.8 mg/mL) to the reagents solution, while pyrazine-containing samples were obtained by conducting the reaction in DMF and using the respective metal acetate salts in an autoclave at 100-150 °C.

### 2.2 Pyrolysis of materials.

The materials were pyrolyzed in a tubular furnace at temperatures between 700 and 1000 °C for 1-5 hours under a N<sub>2</sub> or Ar-H<sub>2</sub> flow. The pyrolysed powders were then structurally and electrochemically characterized.

### 2.3 Cyclic Voltammetry

The electrochemist study of the samples focused in OER and HER. All electrochemical measurements were performed with a Bio-Logic VMP3 potentiostat/galvanostat having a built-in EIS analyzer. The electrochemical activity and stability of catalysts were measured in a three-electrode electrochemical cell using a 3 mm diameter glassy carbon rotating disc electrode (RDE). A platinum wire was used as the counter electrode and Ag/AgCl (3 M KCl) was used as the reference electrode. The catalyst inks were prepared as follows: 3 mg of the sample catalyst was added to 235  $\mu\text{L}$  of  $\text{H}_2\text{O}$ , 235  $\mu\text{L}$  of ethanol, and 300  $\mu\text{L}$  of 5 wt % Nafion solution and then the mixture was dispersed by sonication for 30 min to obtain a homogeneous ink. The electrodes were prepared by depositing 3  $\mu\text{L}$  of the catalyst ink onto the GC disc and drying at room temperature.

The OER measurements were conducted in 1 M KOH electrolyte at 25  $^{\circ}\text{C}$ , with the RDE rotated at 1600 rpm. CV curves were measured in the potential window 0–0.7 V versus Ag/AgCl at a scan rate of 20  $\text{mV s}^{-1}$ . The HER measurements were conducted in 0.5 M  $\text{H}_2\text{SO}_4$  at 25  $^{\circ}\text{C}$  with the RDE rotated at 2000 rpm. Cyclic voltammetry (CV) experiments were performed in the potential window –0.6 to 0 V versus Ag/AgCl with scan rate of 20  $\text{mV s}^{-1}$ .

## 3. Results and Discussion.

### 3.1 Structural characterisation.

The chemical composition of the solids obtained by pyrolysis under  $\text{N}_2$  and  $\text{H}_2$  were identified by X-ray powder diffraction and quantified by the Rietveld method [6]. Table 1 shows the main crystalline phases found for some presentative compositions at different temperatures and atmospheres.

**Table 1.** Phase identification for pyrolyzed  $\text{Co}_{1-x}\text{Fe}_x\text{HPAA}$  samples.

DRX	700 $^{\circ}\text{C}$ ( $\text{N}_2$ )	900 $^{\circ}\text{C}$ ( $\text{N}_2$ )	1000 $^{\circ}\text{C}$ ( $\text{N}_2$ )	850 $^{\circ}\text{C}$ ( $\text{H}_2$ )
<b>FeHPAA</b>	$\text{Co}_2\text{P}_2\text{O}_7$ -type	$\text{Fe}_2\text{P}_2\text{O}_7$ triclinic	$\text{Fe}_2\text{P}_2\text{O}_7$ triclinic	$\text{Fe}_2\text{P}$
<b><math>\text{Co}_{0.5}\text{Fe}_{0.5}\text{HPAA/GO}</math></b>	$(\text{Co}_{0.5}\text{Fe}_{0.5})_2\text{P}_2\text{O}_7$ (monoclinic)	$(\text{Co}_{0.5}\text{Fe}_{0.5})_2\text{P}_2\text{O}_7$ (monoclinic)	$(\text{Co}_{0.5}\text{Fe}_{0.5})_2\text{P}_2\text{O}_7$ (monoclinic)	$\text{Co}_2\text{P} + \text{CoP} + \text{Fe}_2\text{P}$
<b>CoHPAA</b>	$\text{Co}_2\text{P}_2\text{O}_7 + \text{Co}_2\text{P}_4\text{O}_{12}$	$\text{Co}_2\text{P}_2\text{O}_7 + \text{Co}_2\text{P}_4\text{O}_{12}$	$\text{Co}_2\text{P}_2\text{O}_7 + \text{Co}_2\text{P}$	$\text{Co}_2\text{P} + \text{CoP}$

Under a  $\text{N}_2$  atmosphere between 700–1000  $^{\circ}\text{C}$ , CoHPAA decomposes in a mixture of  $\text{Co}_2\text{P}_2\text{O}_7$  and  $\text{Co}_2\text{P}_4\text{O}_{12}$ . Above that temperature mixture of  $\text{Co}_2\text{P}_2\text{O}_7$  and a cobalt phosphide ( $\text{Co}_2\text{P}$ ) is detected. However, the pyrolysis in  $\text{H}_2$ -Ar at 850  $^{\circ}\text{C}$  yields a unique  $\text{Co}_2\text{P}$  compound. For the Fe(II)-containing samples, monoclinic and triclinic  $\text{Fe}_2\text{P}_2\text{O}_7$  were formed under  $\text{N}_2$  after heating the precursors from 700–1000  $^{\circ}\text{C}$ . In  $\text{H}_2$ -Ar, phosphide solid solutions, Co/Fe $_2\text{P}$ , were the only crystalline phases detected. GO or Pyrazine have been added in order to increase the textural properties of the materials.

### 3.2 Cyclic Voltammetry

Figure 1 displays the CV results for the different studied materials.

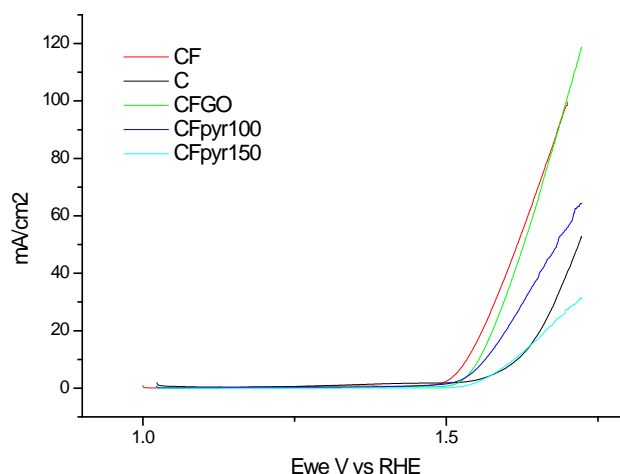


Figure. 1. LSV OER of samples  $\text{Co}_{0.5}\text{Fe}_{0.5}\text{HPAA}$  (CF),  $\text{CoHPAA}$  (C),  $\text{Co}_{0.5}\text{Fe}_{0.5}\text{HPAA\_GO}$  (CFGO),  $\text{Co}_{0.5}\text{Fe}_{0.5}\text{HPAA\_pyrazine}$  at 100 °C synthesized (CFpyr100) and  $\text{Co}_{0.5}\text{Fe}_{0.5}\text{HPAA\_pyrazine}$  at 150 °C synthesized (CFpyr150), all of them pyrolyzed at 850 °C under a  $\text{H}_2$ -Ar flow.

By taking the reference as  $10 \text{ mA cm}^{-2}$ , corresponding to the current drawn by a solar-to-fuel device with about 10% efficiency under an illumination of AM1.5G ("one sun"). the best overpotential obtained is 304mV for  $\text{Co}_{0.5}\text{Fe}_{0.5}\text{HPAA}$ . The addition of GO or pyrazine for the samples do not improve the electrocatalytic properties of the resulting materials, likely due to the fact that the porosity did not increase enough with the amounts GO and pyrazine added. Moreover, CoFe samples exhibit an improvement in terms of overpotential respect the Co sample. Therefore, Co/Fe solid solutions should be further investigated.

#### 4. Conclusions.

$\text{Co}_{1-x}\text{Fe}_x\text{-HPAA}$  metal phosphonates were prepared and pyrolyzed under  $\text{N}_2$  and  $\text{H}_2/\text{Ar}$  flows. The resulting powders were structural and electrochemically characterised by XRD and CV, respectively. The obtained materials possess different structures depending on the temperature and pyrolysis atmosphere. Samples pyrolyzed in  $\text{N}_2$  at 1000 °C are monophasic diphosphates, while phosphides form in  $\text{H}_2/\text{Ar}$  at 850 °C.

Cyclic voltammetry studies indicate that the  $\text{Co}_{0.5}\text{Fe}_{0.5}\text{HPAA}$  sample, pyrolyzed in  $\text{H}_2/\text{Ar}$ , exhibits the best behaviour, but further studies are needed to fully understand the role of graphene oxide and pyrazine.

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